

c/

TRANSMISSION ELECTRON MICROSCOPY AT 2.5 MeV

Gareth Thomas and J. -C. Lacaze

February 1973

Prepared for the U.S. Atomic Energy
Commission under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



c/

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

TRANSMISSION ELECTRON MICROSCOPY AT 2.5 MeV

Gareth Thomas

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and
Department of Materials Science and Engineering, College of Engineering;
University of California, Berkeley, California

and

J.-C. Lacaze

Laboratoire d'Optique Electronique du CNRS
31-Toulouse, France

ABSTRACT

Measurements of penetration on silicon and austenitic stainless steel have been continued using the same criteria as previously reported (G. Thomas, Phil. Mag., 17, 1097, 1968) up to 2.5 MeV using the 3 MeV Toulouse electron microscope. The results show that penetration increases to about 14μ at 2.5 MeV for silicon although the curve starts to flatten out above 1.5 MeV, but no significant gain was found for stainless steel $\approx 2\mu$ at 2.5 MeV). Primary knock-on damage occurs readily in both materials. The critical voltages for 440 silicon and 422 tantalum were measured, and both found to be 1.4 MeV ($\pm 10\text{kV}$).

Attempts to measure the variation of radiation damage with beam voltage in crystalline amino acids as indicated by the fading of diffraction patterns indicated that the damage rates apparently decrease as the voltage is raised to 2.5 MeV. However, it was not possible to determine this variation quantitatively because of difficulties in measuring the absolute values of the critical exposures.

INTRODUCTION

Although the major advantages of high voltage electron microscopy have now received some considerable attention, so far experimental data have been mainly limited to up to 1.2 MeV, e.g. studies of penetration (Dupouy and Perrier 1962-64; Fujita et al. 1967; Thomas 1968; Hale and Henderson-Brown 1970; Uyeda and Nonoyama 1968; Humphries et al. 1971), critical (disappearance) voltage phenomena (Uyeda 1968; Bell 1969; Lally et al. 1970), radiation damage (e.g. Makin 1969; Urban and Wilkens 1972; Thomas et al. 1970; Kobayashi and Ohara 1966, Glaeser 1971; Grubb and Groves 1971; Claffey and Parsons 1972), improvements in resolution of bright field images of defects (Bell and Thomas 1972; Goringe et al. 1972), and applications in materials science and biology (for reviews see for example Dupouy 1968; Cosslett 1970; Bell and Thomas 1972; Fisher 1972).

In 1970 Dupouy et al. published their pioneering work describing the Toulouse 3 MeV microscope. It was anticipated that the advantages which could now be attained would include improvements in penetration. For metallic crystals primary knock-on damage should be observable in heavy metals and critical voltages attainable for a wide range of reflections and crystals. However, knock-on damage limits the applications of very high voltage electron microscopy of inorganic materials. Of significant interest is radiation damage in biological and polymeric specimens since this damage handicaps the attainment of high resolution images of single atoms and molecules, and dynamic observations of living cells. Although stopping power theories predict a decrease in specimen lifetime above 1 MeV, i.e. the radiation damage should not then decrease (e.g. Glaeser 1971), Cosslett 1971) suggested that the electron energy deposited in the sample is less at higher voltages so that a reduction

in radiation damage might then be expected. It is obvious that experimental data on this aspect are sorely needed.

Thus the present paper describes some results which have been obtained up to 2.5 MeV on the Toulouse microscope in which penetration measurements have been continued on Si and stainless steel using the same criteria as described previously (Thomas 1968), determinations of the disappearance voltage for the 440 reflection in silicon and 422 in tantalum were made and attempts were made to measure radiation damage in organic crystals (L-valine, glycine).

EXPERIMENTAL

Thick specimens of epitaxial silicon single crystals (diamond cubic structure) were especially grown for these experiments, so as to contain relatively high densities of stacking faults in order to facilitate the penetration measurements. Foils were prepared by chemical thinning in the usual way. Similarly foils of austenitic stainless steel (face centered cubic structure), which had been heat treated after deformation to contain twins and dislocation pile-ups, were obtained by electro-polishing. Foils of silicon were also prepared from specimens which had been deformed at high temperatures.

Thin specimens of L-valine and glycine suitable for radiation damage experiments were prepared as described by Glaeser (1971). The specimens 500 - 1000Å thick were mounted on thin carbon support films, and the damage estimated by recording the lifetimes (times to destruction) of crystalline diffraction patterns as a function of beam current and accelerating voltage, e.g. Kobayashi and Ohara (1966); Glaeser (1971).

The use of the diffraction pattern rather than the image, facilitates measurements because shorter photographic exposure times are required.

Current densities were estimated by using a Faraday cage placed below the final projector lens (condenser aperture was 200μ , selected area aperture 50μ).

The two main sources of errors in these measurements are: firstly, the determination of the "end-points" of fading which is limited by the time for photographic exposure of the diffraction pattern, (± 5 sec); and, therefore, depends on the photographic sensitivity of the plates at different voltages. Secondly, there may be errors in the current density measurements by the Faraday cage method. At higher energies electron penetration into the cage may occur other than through the cage aperture. Also secondary electron emission can occur inside the cage {see e.g. Claffey and Parsons (1972)}. The magnitude of the error in current measurement due to these factors thus depends somewhat on the accelerating voltage (electron energy). Consequently, it is very difficult to obtain absolute values of the critical exposures (current density times lifetime) at high energies.

RESULTS

a) Penetration

Figure 1 shows the results of the penetration measurements which were all carried out above 1 MeV using the same objective aperture size (20μ) with the foils oriented to excite a low order systematic set of reflections (220 for silicon, 111 for stainless steel). As in the previous experiments (Thomas 1968) the penetration limit was taken to occur at that thickness at which interference fringes at faults (Si) or twins (steel) were destroyed by absorption, care being taken to ensure

proper focusing and maximum contrast at each stage of measurement. Since the Bragg angle changes with voltage, tilting is necessary to maintain optimum conditions. Typical examples of the diffracting conditions are shown in Figs. 2b and 3b. The foil thickness can be found accurately from the trace of the fault plane, foil orientation (from the Kikuchi pattern), and the tilt angles. Figure 2 shows an example of the method used: a) shows a stacking fault in silicon for which all fringes are visible at 2μ thickness at 1.5 MeV. The fault is then traversed into the thicker regions until the fringes are no longer visible (it is necessary to record these end points photographically) keeping the orientation constant. Magnifications used for obtaining the images were $5,000\times$ (accurate to 5%). In Fig. 2c there are still 6-8 fringes visible at 2.5 MeV at a thickness of 14μ (open circles, Fig. 1). Experience has shown that this condition corresponds to the useful practical limit for routine microstructural characterization. Whilst channelling can increase penetration, the resolution in the channelling mode is poor (Bell and Thomas 1972) and so this orientation is not of significant practical interest.

Figure 3 shows an example of the thickness limit at 2.5 MeV for stainless steel. The twin fringes are damped out but the inclined dislocations still show about three oscillations at each foil surface. The resolution is good under these conditions, although screen visibility is poor and longer than normal exposure times (5-10 secs) are necessary to obtain such images. The thickness at this stage is about 2.2μ . It will be noted that there is no significant gain in penetration for stainless

steel between 1 MeV and 2.5 MeV.* There is also no significant depth dependence of the resolution of the dislocation lines (top-bottom effect, Hashimoto 1964).

After these results were obtained, Humphries (1972) published a theoretical paper discussing the optimum orientations and voltages for penetration in metals taking aluminum, iron and gold as representative of light, medium and heavy elements. He suggested that 3 MeV is the maximum voltage for light elements, 2 MeV for medium weight metals and 1 MeV for heavy metals. These results are in general agreement with the present experimental data especially for light elements, although Humphries' theory appears to be more optimistic for medium weight metals than is actually observed (Fig 1). However, at these high voltages knock-on damage and associated effects alter the microstructure e.g. formation of clustered point defects, (Figs. 2,3), and decoration of dislocations (Goringe et al. 1972), so that apart from investigations of radiation damage and its applications for reactor technology, accelerating voltages above 1 to 2 MeV may not be very useful for metallurgical research.

b) Measurement of Critical Voltages

The critical voltages for 440 silicon and 422 tantalum were measured both by using the Kikuchi line and divergent beam techniques (Bell 1970; Lally et al. 1972) and the voltage calibrated by taking low magnification Kikuchi patterns (Thomas 1970). The values obtained were, coinci-

* This result has been confirmed using an independent method by Drs. Jouffrey and Reynaud at Toulouse.

dentally, the same viz., Si(440) 1.4 MeV, Ta(422) 1.4 MeV, to within experimental error (± 10 kV).

Observations of dislocations and radiation induced defects in Silicon in the 440 critical voltage condition confirmed that there is a gain in contrast (due to the low background), resolution, and simplicity of the image {Bell and Thomas (1972), Goringe et al. (1972)}.

c) Radiation Damage in Amino Acids

Measurements of the relative current densities vs. lifetime of specimens corresponding to the complete fading of the diffraction patterns of valine and glycine at each voltage confirmed that the lifetimes are independent of dose rate (Glaeser 1971) so that heating effects are negligible in the damaging processes.

Unfortunately, it was not possible to make absolute measurements of the critical exposures as a function of voltage above 1 MeV. However, the relative critical exposures apparently increase up to 2.5 MeV indicating that the rate of radiation damage may decrease with increasing beam energy. This possibility requires further examination and it is clear that more experimental and theoretical research is urgently needed on this problem. Naturally further experimental work is continuing at Toulouse (G. Dupouy private communication) and at Berkeley where Linac experiments are being planned (Glaeser et al. 1973). If decreases in radiation damage continue to higher voltages, it will be necessary to evaluate whether or not very high voltage, high resolution ($\approx 2\text{\AA}$) electron microscopes (5-10 MeV) may be desirable for future research, in spite of their enormous costs.

SUMMARY

Electron microscopy above 1 MeV appears to be particularly promising for the study of organic materials because of the apparent reduction in radiation damage and, consequently, improved resolution. It is essential for more research to be done to check this possibility. Experimentally accurate methods for determining critical exposures for complete damage are needed. More theoretical work is also required to analyse the scattering and damage processes.

In inorganic materials the gain in penetration with voltages above 1 MeV appears to be significant only for light materials such as silicon, and this may be important for semiconductor research. Critical voltages can be measured for a wide range of reflections and materials if a 3 MeV microscope is available. Knock-on damage in crystals can also be investigated directly.

ACKNOWLEDGEMENTS

Cooperation and advanced planning involving a large number of people have made this research possible. G.T. would especially like to thank Professors G. Dupouy and F. Perrier, and Dr. B. Jouffrey for their generous allocation of precious time on the 3 MeV microscope at Toulouse and the untiring assistance of Messers. Durieu, Seguela and their staff, for facilitating operation of the microscope.

Dr. G. Schwuttke of IBM, New York kindly provided the faulted silicon crystals and Miss M. Robson prepared the foils from these. Dr. R. M. Glaeser provided the biological samples and much helpful discussion. G. T. also acknowledges helpful discussions on the problems of

-9-

high energy irradiations with Dr. T. F. Budinger. G. T. thanks the Guggenheim Foundation for the award of a Fellowship, and also acknowledges the sabbatical leave from the University of California, Berkeley, U.S.A. This work was done under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

- Bell, W. L. (1969) "Dynamical Theory of Critical Voltages", Micron 1, 289.
- Bell, W. L. (1970) "Determination of Critical Voltages in Crystals", Harwell HVEM Conference, 35.
- Bell, W. L. and Thomas, G. (1972) Electron Microscopy and Structure of Materials, Ed. G. Thomas, University of California Press, 23.
- Claffey, W. J. and Parsons, D. F. (1972) "Electron Diffraction Study of Radiation Damage in Coronene", Phil. Mag. 25, 637.
- Cosslett, V. E. (1970) "Recent Progress in High Voltage Electron Microscopy", Modern Diffraction and Imaging Techniques in Materials Science, North Holland Press, 341.
- Coslett, V. E. (1971) reported at the USA-Japan Seminar on High Voltage Electron Microscopy, Honolulu, Hawaii.
- Dupouy, G. and Perrier, F. (1962) "Microscope Electronique Fonctionnant Sous Une Tension d' Un Million de Volts", J. Microscopie 1, 167.
- Dupouy, G. and Perrier, F. (1964a) "Etude des Substances Cristallisees par Microscopie et Diffraction Electroniques Sous 1 Million de Volts. Application aux Metaux et aux Alliages", J. Microscopie 3, 233.
- Dupouy, G. and Perrier, F. (1964b) "Observation of Metals and Alloys Under 1 MeV", Compt. Rend., 258, 4213.
- Dupouy, G., Perrier, F. and Durrieu (1970) "Microscope Electronique 3 Million de Volts", J. Microscopie 2, 575.
- Dupouy, G. (1968) "Electron Microscopy at Very High Voltage", Adv. Opt. Electron Microsc. 2, 167.
- Fisher, R. M. (1972) Electron Microscopy and Structure of Materials, Ed. G. Thomas, University of California Press, 60.
- Fujita, H., Kawasaki, Y., Furubayashi, E., Kajiwara, S. and Taoka, T. (1967) "Metallurgical Investigations With a 500kV Electron Microscope", Jap. J. Appl. Phys. 6, 214.
- Glaeser, R. M. (1971) "Limitations to Significant Information in Biological Electron Microscopy as a Result of Radiation Damage", J. Ultrastr. Res. 36, 466.
- Glaeser, R. M., Kuo, I., Howitt, D. G. and Thomas, G. (1973) "Electron Irradiation Damage in Biological Materials as a Function of Energy" (in preparation).

Goringe, M. J., Hewat, E. A., Humphries, C. J. and Thomas, G. "Defect Contrast and Resolution in High Voltage Electron Microscopy", Proc. 5th European Congress on Electron Microscopy 1972, 538.

Grubb, D. T. and Groves, G. W. (1971) "Rate of Damage of Polymer Crystals in the Electron Microscope" Phil. Mag. 24, 815.

Hale, K. F. and Henderson-Brown, M. (1970)

Micron 1, 434.

Hashimoto, H. (1964) "Energy Dependence of Extinction, Distance and Transmissive Power for Electron Waves in Crystals", J. Appl. Phys. 35, 277.

Humphreys, C. J. (1972) "The Optimum Voltage in Very High Voltage Electron Microscopy", Phil. Mag. 25, 1459.

Humphreys, C. J., Thomas, L. E., Lally, J. S. and Fisher, R. M. (1971) "Maximizing the Penetration in High Voltage Electron Microscopy", Phil. Mag. 23, 87.

Kobayashi, K. and Ohara, M. (1966) "Voltage Dependence of Radiation Damage to Polymer Specimens", Proc. 6th Intl. Congress Electron Microscopy" (Kyoto) 579.

Lally, J. S., Humphreys, C. J., Metherell, A. J. F. and Fisher, R. M. (1972) "Critical Voltage Effects in High Voltage Electron Microscopy", Phil. Mag. 25, 321.

Makin, M. J. (1969) "A Simple Theory of Loop Formation and Enhanced Diffusion in Crystals Examined by High Voltage Electron Microscopy", Phil. Mag. 20, 1133.

Rohrlich, F. and Carlson, B. C. (1954) "Positron-Electron Differences in Energy Loss and Multiple Scattering", Phys. Rev. 93, 38.

Thomas, G. (1968) "Electron Microscopy at High Voltages", Phil. Mag. 17, 1097.

Thomas, G. (1970) Modern Diffraction and Imaging Techniques in Materials Science, North Holland Press, 159.

Thomas, L. E., Humphreys, C. J., Duff, W. R. and Grubb, D. T. (1970) "Radiation Damage of Polymers in the Million Volt Electron Microscope", J. Radiation Effects 3, 89.

Urban, K. and Wilkens, M. (1972) Electron Microscopy and Structure of Materials, Ed. G. Thomas, University of California Press, 929.

Editor -
please complete
dile

Uyeda, R. (1968) "Dynamical Effects in High Voltage Electron Diffraction", Acta. Crystallogr. A24, 175.

Uyeda, R. and Nonoyama, M. (1968), "The Observation of Thick Specimens by High Voltage Electron Microscopy. II Experiment With Molybdenite Films at 50-1200kV", Jap. J. Appl. Phys 7, 200.

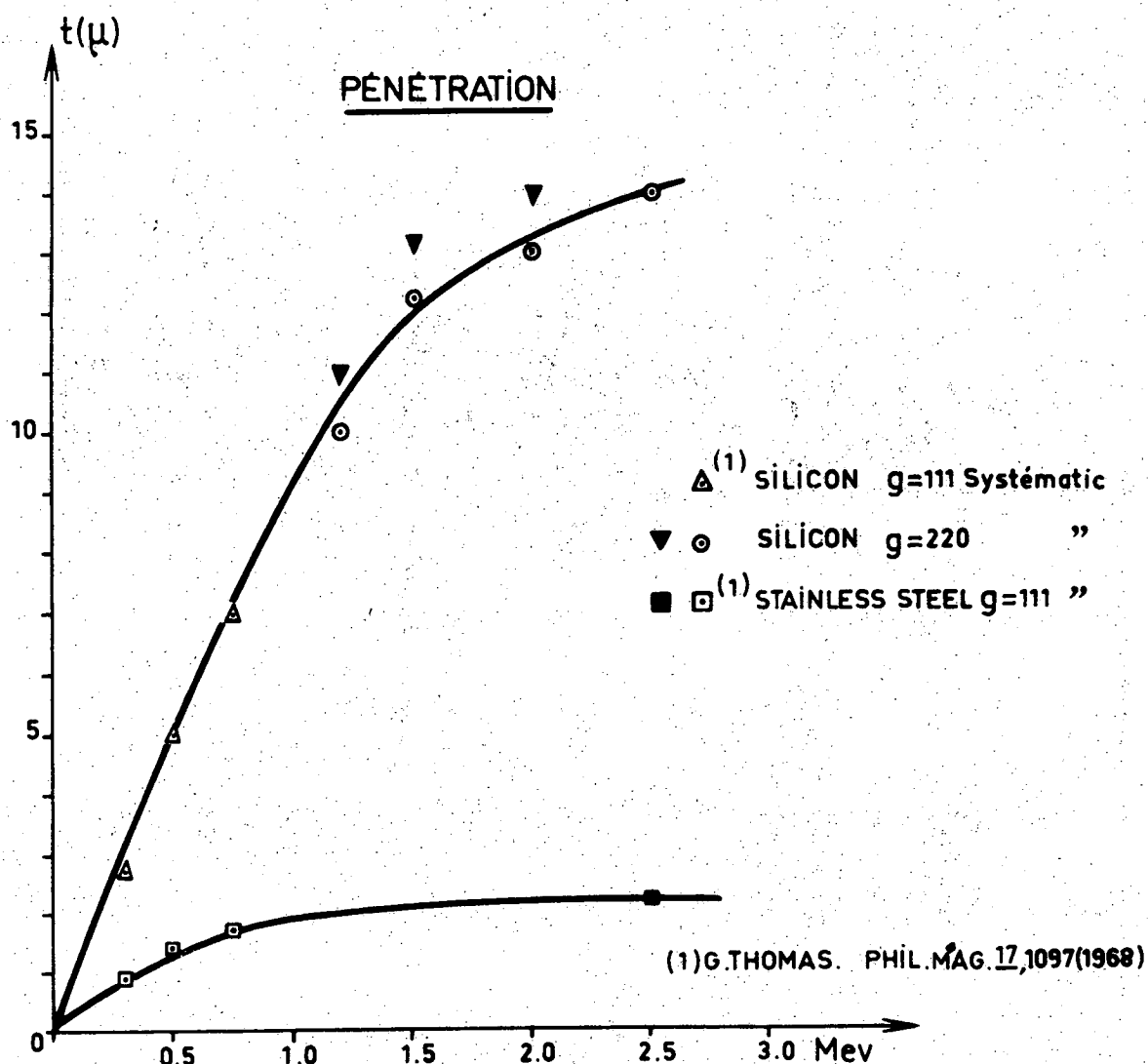
FIGURE CAPTIONS

Fig. 1. Penetration data obtained for silicon and stainless steel.

Open circles correspond to thicknesses for which up to six fringes are visible at stacking faults. Closed triangles correspond to total loss of fringes. The open triangle at 2.5 MeV corresponds to the thickness for which all fringes are just visible. All results obtained for systematic reflections as shown in Figs. 2,3.

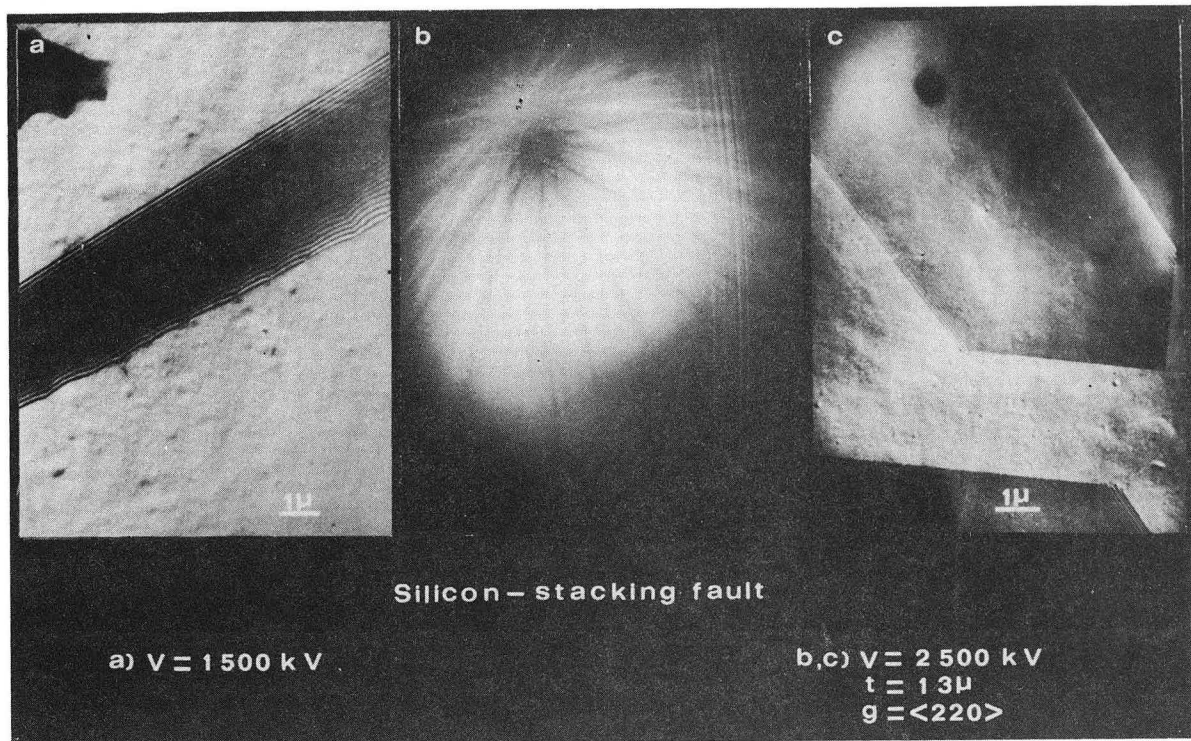
Fig. 2. Examples of the fringe technique for obtaining the data of Fig. 1. (b) shows the orientation of the systematic 220 set of reflections - bright field images a, c obtained for $g = 220$ with s slightly positive. Thicknesses obtained from the fault traces.

Fig. 3. Similar to Fig. 2 but for austenitic stainless steel. (a) bright field image $g = 111$ (s slightly positive). Notice good dislocation resolution but no fringe contrast at the twin interfaces; irradiation damage is evident. Thickness 2.2μ at 2.5 MeV.



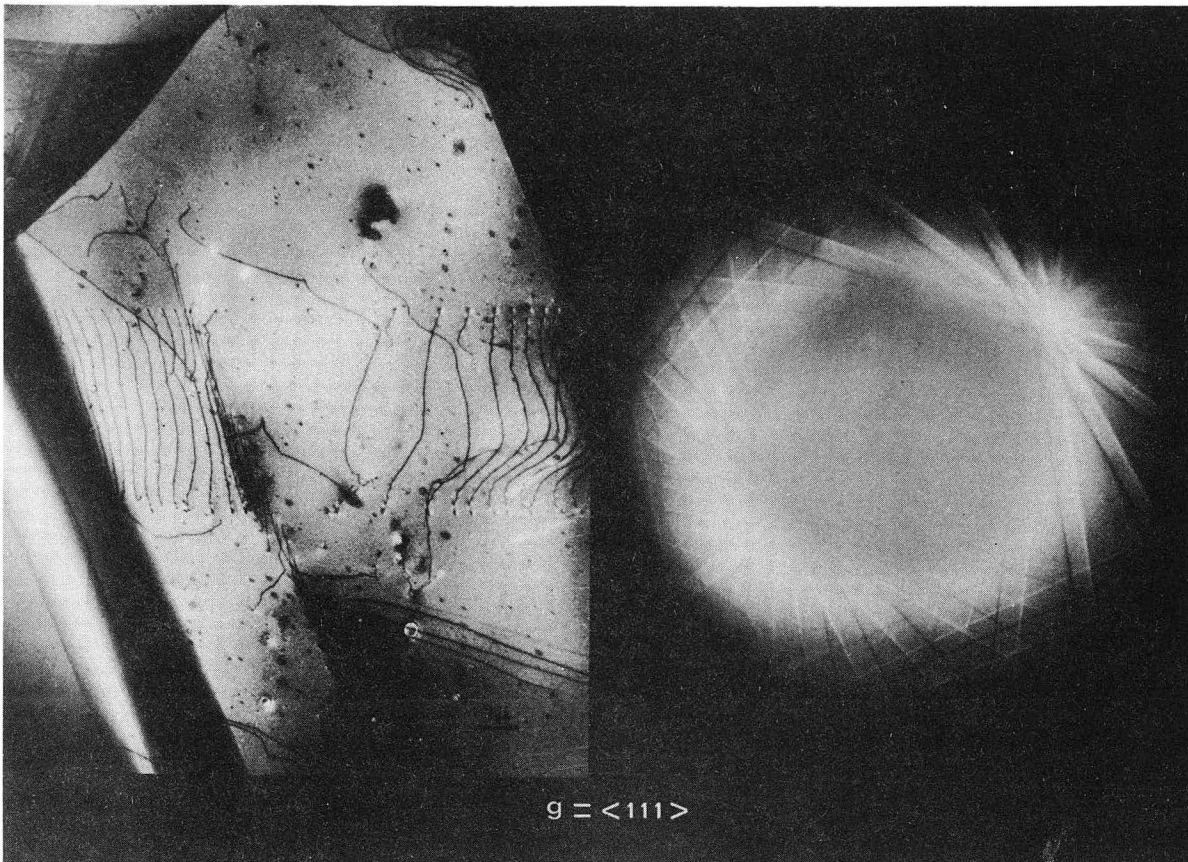
XBL 728-6771

Fig. 1



XBB728-4086

Fig. 2



XBB 728-4087

Fig. 3

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720